

UNCLASSIFIED

AD 410358

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY DDC
AS AD No. 410358

410358

N-63-4-3

OFFICE OF NAVAL RESEARCH

TECHNICAL REPORT

NO. 4

Contract Nonr - 3707(00)

Recovery of Defects Following Deformation of

High Purity Cadmium at 78° K

F. R. Stevenson and H. R. Peiffer

RIAS
7212 Bellona Avenue
Baltimore 12, Maryland

July, 1963

Reproduction in whole or in part is permitted for any
purpose of the United States Government.

I. INTRODUCTION

It is well established that point and line defects are created during low temperature plastic deformation of metals and that these defects will affect structure sensitive properties. It is generally held that point defects are produced by the motion of dislocations. Two prominent mechanisms for the production of point defects during cold-work depend on the motion of jogged dislocations - the jogs being formed either by dislocation intersections or possibly lattice vibrations ^{1, 2}. Dislocation density also increases during plastic deformation.

Upon annealing cold-worked metals, appreciable decreases in electrical resistivity and other defect sensitive properties have been observed. This recovery phenomena has been associated with the migration of defects to sites where their effect is either lessened or entirely removed.

It is now recognized that the presence of impurity atoms can affect the recovery process. Damask and Dienes³ have made some calculations which show that the experimentally determined activation energy for motion of vacancies (E_M) in impure metals can significantly deviate from the true value due to the vacancy-impurity binding energy (B). According to their results, the observed motion energy will vary between E_M and $E_M + B$, the former being obtained only for extremely pure metals, the latter for heavily doped metals. Moreover, at intermediate impurity concentrations,

the recovery curves are expected to deviate from pure exponential behavior due to a temperature dependent effective motion energy. Thus, in employing recovery measurements to determine the energy for vacancy migration, it is necessary to use very pure material in order to obtain reliable results. In this paper, some recovery measurements on high purity cadmium will be presented and compared to previous results on less pure cadmium⁴.

II. EXPERIMENTAL PROCEDURE

The specimens were 1 mm polycrystalline cadmium wire obtained from Cominco Products with a stated impurity content of less than 0.001%. Specimens of this wire (hereafter referred to as 59 cadmium) were analyzed in an emission spectrograph by another laboratory and the results are shown in Table I. The 59 cadmium has a total impurity content much less than 10 parts per million. For comparison, the spectrographic analysis of some less pure cadmium (hereafter referred to as 49 cadmium) we previously reported on is also included in Table I.

The specimens were annealed at 100°C for 2 hours in an argon atmosphere and chemically polished in the manner previously reported⁴. All resistances were measured potentiometrically at liquid nitrogen temperature to a precision of .004%.* A dummy specimen immersed in the liquid nitrogen allowed temperature fluctuations to be monitored and served as a means of normalizing the resistance measurements to a common

*A more detailed description of the experimental details is to be found in Reference 4.

temperature. Elongation of approximately 6% was accomplished in the low heat capacity apparatus shown in Figure 1 which was also used for specimen transport during annealing. The apparatus is a slightly modified version of the one formerly used⁴. The changes permit easier mounting and better definition of the deformed section of the wire.

The annealing was performed by transferring the specimen rig to a liquid at the desired temperature. Freon 13 was used for an annealing bath from 88°K to 188°K while Dow 200 series silicon fluid was used from 198° to 278°K. Considerable difficulty was encountered at the lower range of the latter bath due to freezing of the oil which made the obtaining of square temperature pulses difficult and interfered with the resistance measurements. Otherwise, the temperature-time behavior characteristics, as determined by using the specimen as a resistance thermometer, were close to an ideal square pulse. The previously noted temperature spikes, superimposed on the square pulse, were still prevalent at the lower annealing temperatures and a small correction was made for this effect in the manner discussed earlier⁴.

III. RESULTS

Figure 2 presents the data obtained from the sequential isotherm method. In this method, previously referred to as method A*, the ratio of the slopes of adjacent isotherms is used to derive the activation energy

*A full description of methods A and B can be found in Reference 4.

for defect motion. The inconsistent behavior of the 198°K isotherm is attributed to the previously mentioned difficulties with the annealing bath.

Recovery data on 59 cadmium wire obtained by the relaxation method previously referred to as method B*, are shown in Figure 3. Data were not obtained at 198°K due to annealing bath difficulties. The initial resistance for all isotherms, each of which corresponds to a different specimen, were arbitrarily normalized to an initial resistance of 2122.35 micro ohms, to account for geometry differences among the specimens. The actual resistances were, with one exception, within five percent of the group average. The 268°K isotherm had an initial resistance about twenty-four percent higher than the average but showed behavior consistent with the others.

The anomalous behavior of the $228\text{--}238^{\circ}\text{K}$ isotherms was of some concern. Measurements at these particular recovery temperatures were repeated numerous times. Although additional measurements in any other temperature region agreed very well with prior determinations, the scatter of the data points from experiment to experiment was larger at these temperatures than expected from the precision of the resistance measurements. No complete explanation can be offered for this behavior at the moment although it is believed incipient recrystallization may in part be responsible for it. It is

* A full description of methods A and B can be found in Reference 4.

proposed that slight differences in specimen grain orientation and amount of deformation disrupted the start of the recrystallization process thereby causing the scatter. Thus, the normalization procedure inherent in method B may not be strictly legitimate. However, this limitation does not appear too severe since the data are for the most part internally consistent and give results which, as will be seen, compare favorably with the results of method A. The resistance rise associated with the 278°K isotherm and the cross-over between the $258\text{-}268^{\circ}\text{K}$ isotherms are due to resistivity anisotropy in the recrystallized specimens as previously reported⁴.

The relaxation data in Figure 3 is shown in Figure 4 in the form of a \ln time vs reciprocal of absolute temperature plot for the same degree of recovery (i.e. same resistance). If the recovery is a thermally activated rate process, the data will fall on straight lines from whose slope the activation energy of the migrating defect can be obtained. The straight lines in Figure 4 represent a least square fit of the data and the resulting energies are shown.

IV. DISCUSSION

In order to better evaluate the effects of impurities on the annealing processes it is advisable to obtain an annealing spectrum for cadmium in various stages of purity. Following Magnuson et al⁵ the annealing spectrum

is defined in terms of the ratio of the observed property change during an annealing interval to the energy change corresponding to the same degree of completion of the annealing process. This ratio is then plotted against the average energy of the observed process. These average energies were found from our data by plotting the results of method A as a function of temperature and drawing a suitable curve through these points. From this curve suitable energy values were obtained for any temperature. Otherwise, the method employed by us was that outlined by Magnuson et al⁵. Determining the energy as suggested by the latter paper resulted in exactly the same spectrum as long as the frequency factor was relatively constant.

Application of the above analysis to the sequential isothermal annealing data (method A) obtained in this investigation gave the curve shown in Figure 6. Annealing peaks A and B appear at approximately 0.24 and 0.300 ev. The defect spectrum of 49 cadmium investigated previously, which is also shown in Figure 6, has the same general shape with the peaks broadened, shifted to higher energies, and reduced in magnitude by approximately a factor of three. In the previous investigation the A' peak was attributed to vacancy recovery.

The peaks A and A' are obviously the most predominant feature of the recovery spectra. If we associate them with the migration of the same defect, then the difference in migration energy can be attributed to the effect of impurities. According to Dienes and Damask³, the true motion energy of a vacancy will only be observed in very pure material. From our data we

may estimate a lower limit on the binding energy of a vacancy to an impurity from the difference in energy between the peaks A and A'. The results of the recovery spectrum analysis are shown in Table II. At present the best value for the migration energy of a vacancy in cadmium would be approximately 0.24 ev although experiments on purer material may possibly lower this result. A lower limit on the impurity binding energy is seen to be approximately 0.09 ev. Since the 49 cadmium has five impurities present at about the same concentration, it is not clear to which impurity this binding energy can be attributed.

Following Magnuson et al ⁵, the values of the frequency factor $\ln(A/a)$ obtained from the analysis have been used to calculate the average number of jumps to annihilation on the assumption that $A = 10^{13}/\text{sec}$. (See Table II) Since the number of jumps for annihilation is much larger in the purer cadmium, it is obvious that the presence of impurities affects the mechanism of recovery.

The migration energies shown in Figure 4 obtained from method B are consistent with the above results in that a distribution of energies monotonically increasing with temperature, of the correct magnitude, and displaced below the corresponding values for the 49 cadmium are found. However, since the method B approach assumes that a unique activation energy exists over a wide temperature range, it is impossible to extract any additional significance.

V. CONCLUSIONS

1. The recovery in pure cadmium is more peaked around certain activation energies than less pure cadmium. Impurities tend to make the annealing a more continuous process with a wide range of activation energies.
2. The energy of motion of a vacancy in cadmium is approximately 0.24 ev.
3. The binding energy of a vacancy to some average impurity has a lower limit of 0.09 ev.
4. Impurities are the important annihilation centers for vacancy recovery in cadmium.

REFERENCES

1. Kuhlmann-Wilsdorf, D. and Wilsdorf, H.G.F., Acta Met., 10, 5 (1962).
2. Peiffer, H.R., Acta Met., 11, 435 (1963).
3. Damask, A.C. and Dienes, G.J., Phys. Rev., 120, 99 (1960).
4. Stevenson, F.R. and Peiffer, H.R., J. Appl. Phys., Sept. 1963.
5. Magnuson, G.D., Palmer, W. and Koehler, J.S., Phys. Rev., 109, 1990, (1958).

Table I. Impurity Concentration in Parts per Million (ppm)
for Cadmium Specimens

Sample Impurity	49 Cadmium Spectrographic Analysis	59 Cadmium	
		Spectrographic Analysis	Manufacture's Analysis
Si	10	<1	
Ag	10	<1	
Cu	3	<1	.5
Zn			
Pb	3	<1	1
Fe	10	<1	1
Al	10		
Mg	10	<1	

Table II
Summary of Recovery Parameters for Cadmium

Material	Peak Temperature (°K)	Peak	E_M (ev)	$\ln A/a$	a
59 Cadmium	138	A	0.240	14.11	7×10^6
59 Cadmium	158	B	0.300	13.70	1×10^7
49 Cadmium	138	A'	0.340	22.68	1×10^3
49 Cadmium	168	B'	0.395	21.72	4×10^3

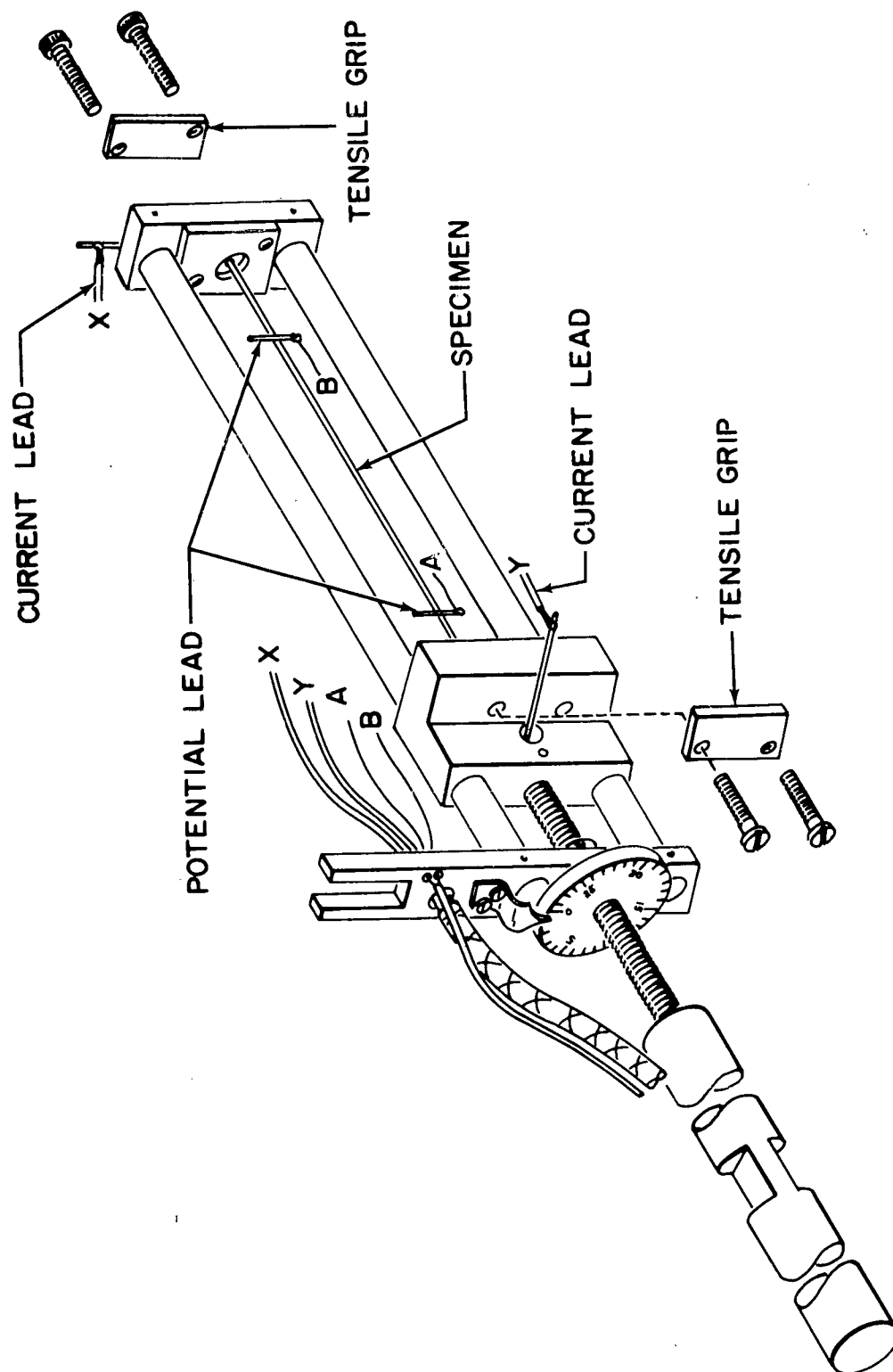


FIGURE 1. THE TENSILE DEFORMATION APPARATUS DESIGNED FOR
THE DEFORMATION AND RECOVERY OF CADMIUM.

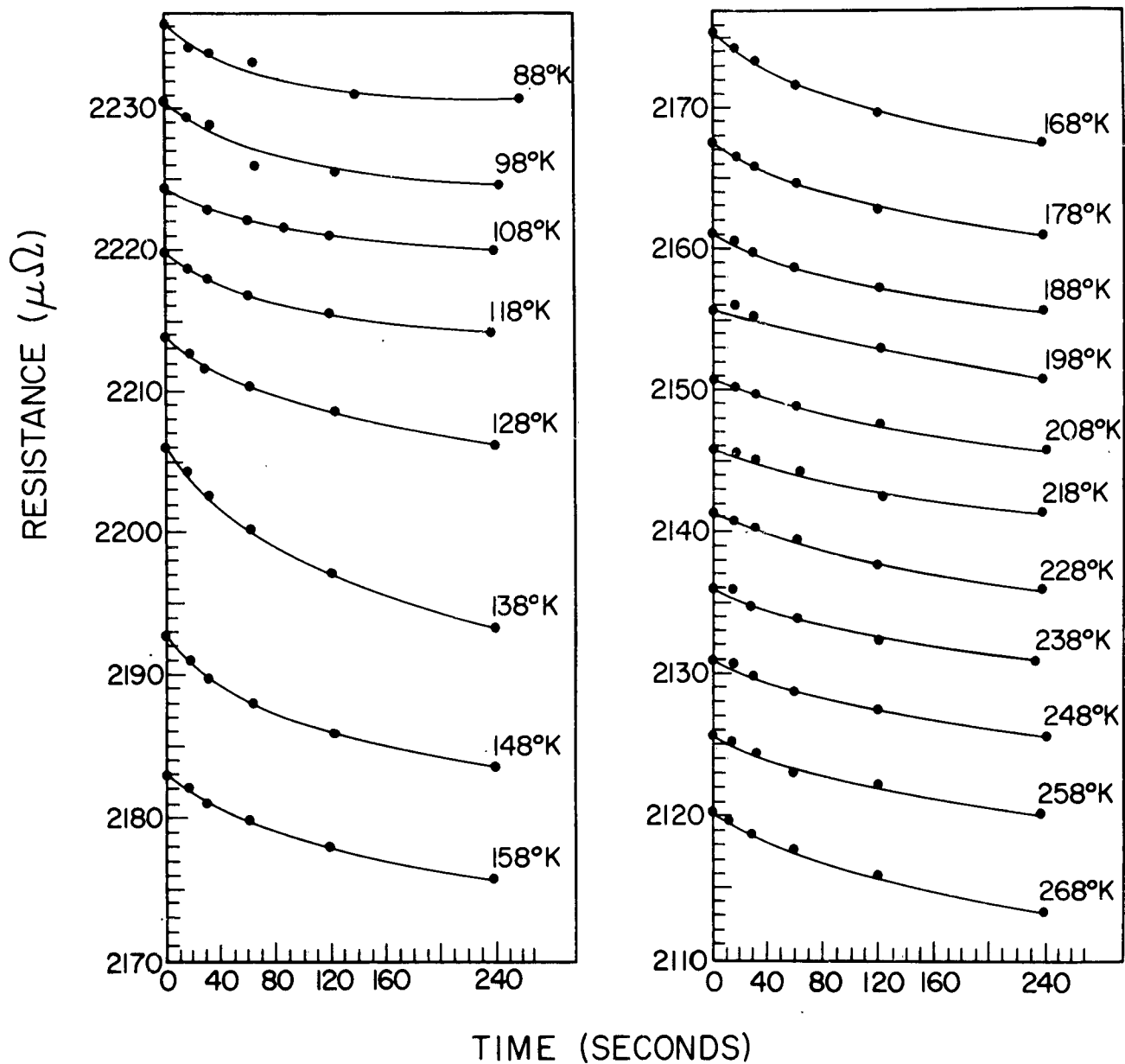


FIGURE 2. THE RESISTANCE TIME PLOTS FOR RECOVERY IN A DEFORMED CADMIUM SPECIMEN. METHOD A.

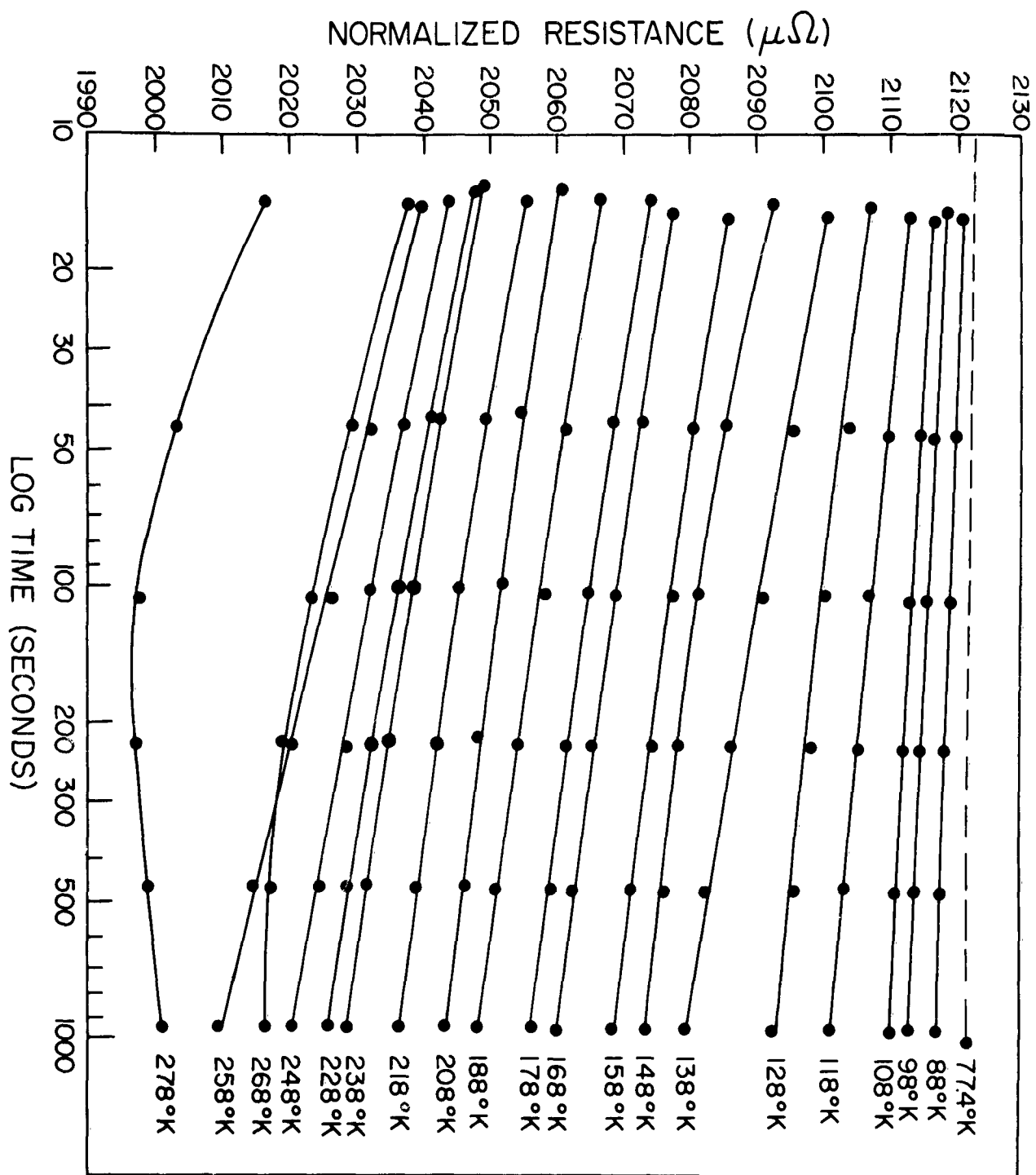


FIGURE 3. NORMALIZED RESISTANCE ISOTHERMS AS A FUNCTION OF TIME FOR DEFORMED CADMIUM SPECIMENS, METHOD B.

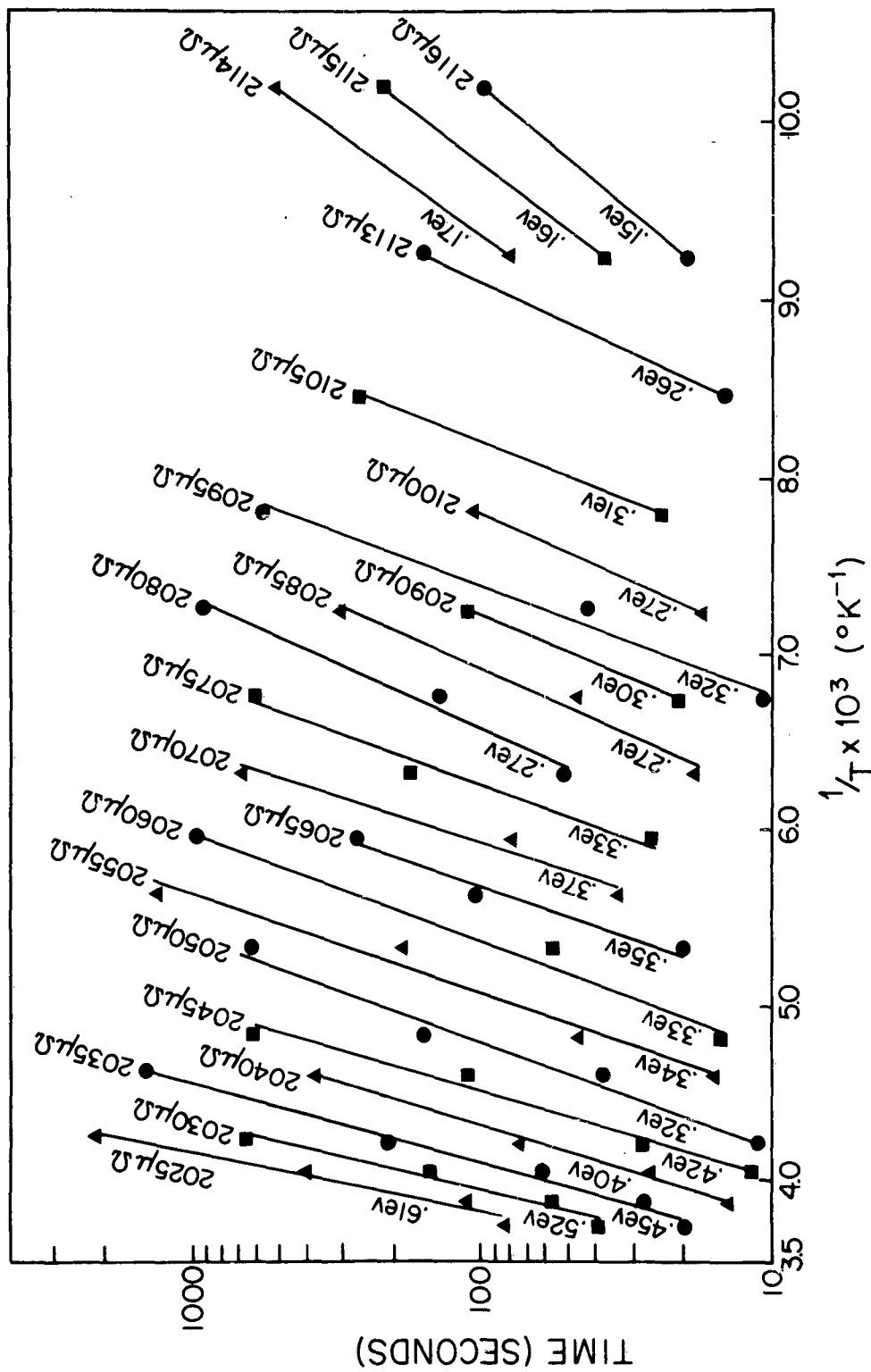


FIGURE 4. LOG TIME TO REACH A RESISTANCE LEVEL AS A FUNCTION OF RECIPROCAL ABSOLUTE TEMPERATURE. THE RESISTANCE LEVEL IS NOTED FOR EACH PLOT AS THE UPPER NUMBER WHEREAS THE LOWER NUMBER DENOTES THE ENERGY OBTAINED FROM THE SLOPE OF THE CURVE. METHOD B.

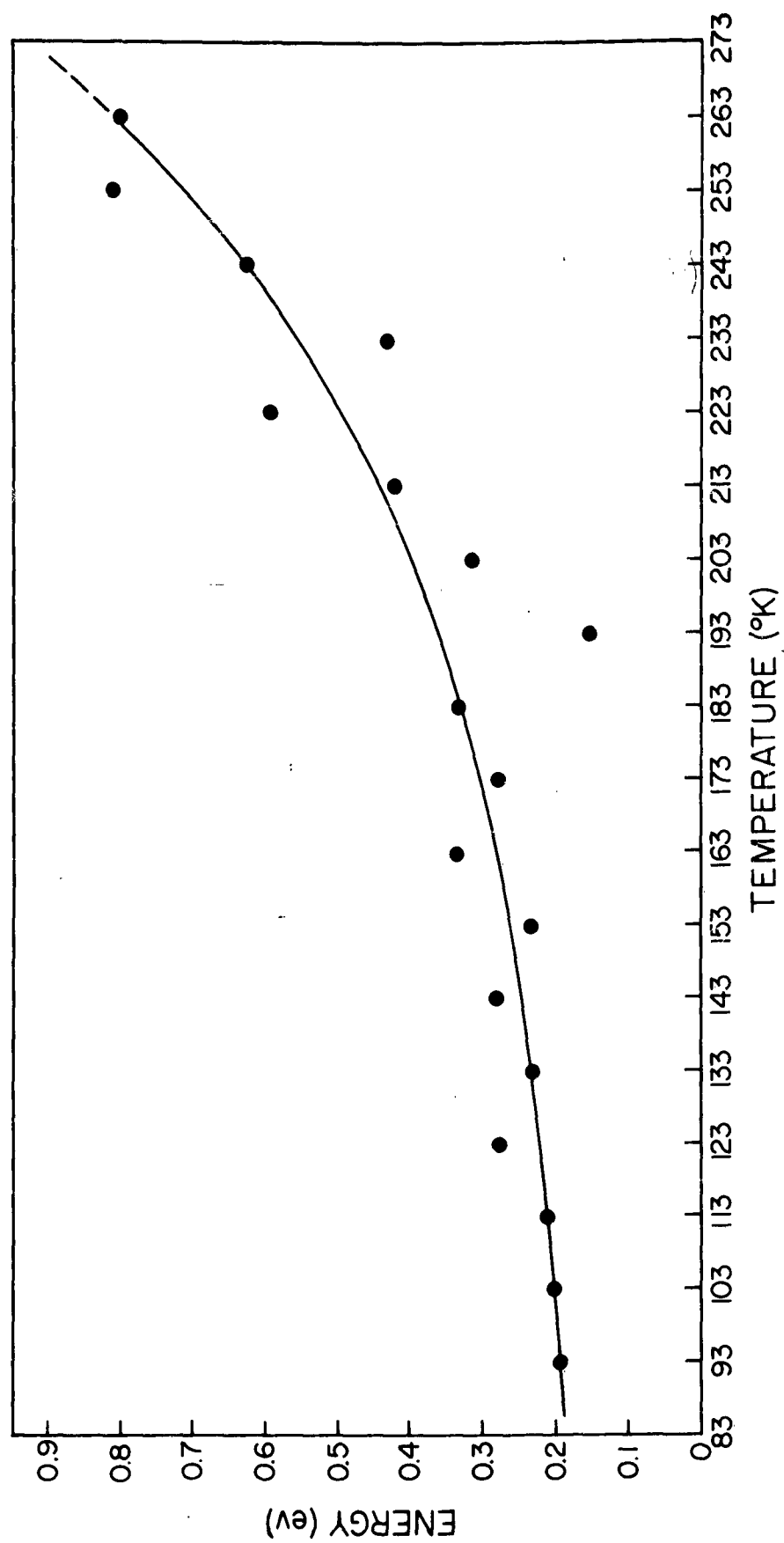


FIGURE 5. ENERGIES OBTAINED AS A FUNCTION OF TEMPERATURE.

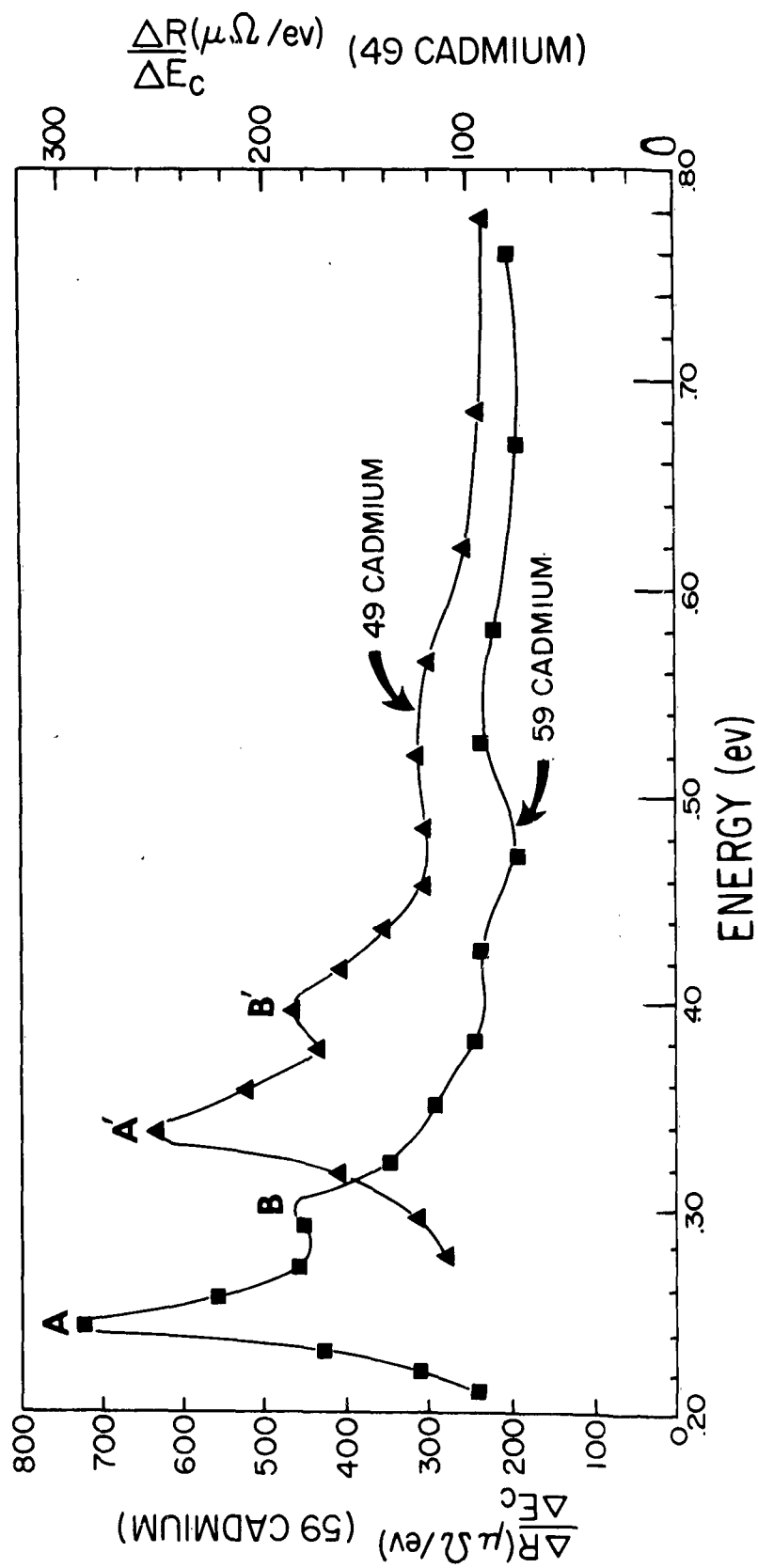


FIGURE 6. INITIAL RECOVERY SPECTRUM OF CADMIUM IN TWO GRADES OF PURITY. NOTE THE TWO ORDINATE SCALES.